

Review

Advances in the pectin production process using novel extraction techniques: A review



Lanrewaju Ridwan Adetunji*, Ademola Adekunle, Valérie Orsat, Vijaya Raghavan

Bioresource Engineering Department, McGill University, 21111 Lakeshore, Sainte-Anne-de-Bellevue, QC H9X 3V9, Canada

ARTICLE INFO

Article history:

Received 5 May 2016

Received in revised form

4 August 2016

Accepted 7 August 2016

Available online 8 August 2016

Keywords:

Pectin

Food hydrocolloids

Solid-liquid extraction

Mass transfer

Novel food processing technologies

Scalability

Chemical compounds:

Pectin (PubChem CID: 441476)

D-galacturonic acid (PubChem CID: 439215)

Cellulase (PubChem CID: 58863022)

Hydrochloric acid (PubChem CID: 313)

ABSTRACT

The heteropolysaccharide known as pectin has found a myriad of functional and nutritive uses within the food and, increasingly, in other related industries. Extraction is a critical unit operation in recovering this compound from its *in situ* state in the cell walls of various plant-based food processing side streams. Although well established, growing demand has exposed certain inadequacies of the mainstream pectin extraction technique—notably efficiency and product consistency, thus prompting research interest towards ameliorating the process by an adoption of a number of novel technologies. Microwave and ultrasound energy appear to be the more likely candidates, but so are enzymatic-augmentation of the extraction process and the use of subcritical water to replace acidified water as solvent, among others. Yet this paper takes an objective approach in evaluating these new methods; for all their advantages, high cost, amidst other drawbacks, still prohibits their use in industry. Furthermore, optimization of process parameters are crucial to better understanding the chances of process scale-up, and this has been the current stage of efforts in the area. The present review discusses the nuances involved in using these non-conventional technologies for its extraction, including advantages and drawbacks. Prospects of their industrial integration are also conjectured.

© 2016 Elsevier Ltd. All rights reserved.

Contents

1. Introduction	240
2. Novel techniques for pectin extraction	241
2.1. Enzyme-assisted extraction (EAE)	243
2.1.1. Underlying principles and mechanisms	243
2.1.2. Operational issues for enzyme-assisted extraction	243
2.1.3. Benefits and drawbacks of enzyme-assisted extraction	244
2.2. Subcritical water extraction (SWE)	244
2.2.1. Underlying principles and mechanisms	244
2.2.2. Operational issues for subcritical water extraction	245
2.2.3. Benefits and drawbacks of subcritical water extraction	245
2.3. Microwave-assisted extraction (MAE)	245
2.3.1. Underlying principles and mechanisms	245
2.3.2. Operational issues for microwave-assisted extraction	245
2.3.3. Benefits and drawbacks of microwave-assisted extraction	247
2.4. Ultrasound-assisted extraction (UAE)	247
2.4.1. Underlying principles and mechanisms	247
2.4.2. Operational issues for ultrasound-assisted extraction	247

* Corresponding author.

E-mail address: lanre.adetunji@mail.mcgill.ca (L.R. Adetunji).

2.4.3. Benefits and drawbacks of ultrasound-assisted extraction	248
3. Future perspectives and concluding remarks	248
Acknowledgement	248
References	248

1. Introduction

Following their isolation, many naturally-synthesized cellular components of plants, animals, and microorganisms help meet some human nutritive and functional needs (Puri, Sharma, & Barrow, 2012). A number of these useful compounds occur as biopolymers, mainly polysaccharides and a few proteins (collectively called hydrocolloids, being water-loving polymers). Pectin is a native polysaccharide in the cell wall and middle lamellae of many land-growing plants, especially those of fruits and vegetables. Historically, the compound was dubbed 'pectic acid' from the Greek word *πηχτες*, meaning coagulated material, by the French scientist Henri Braconnot, who first isolated pectin from vegetables in 1825 (Muzzarelli et al., 2012; Yanakieva, Kussovski, & Kratchanova, 2012). Although ubiquitous in the planta, pectin in citrus, apple, sugar beet and sunflower are considered of special industrial interest (Table 1). This is due to the availability of the biomasses and the physicochemical quality presented by their pectins. Moreover, the properties of extracted pectin are known to vary with the plant source, and the extraction and post-extraction treatment conditions.

The sugar acid, D-galacturonic acid (GalA)—an oxidized form of D-galactose, constitutes the main monomeric unit of the rather complex pectin molecule. The GalA units are linked by α -1 \rightarrow 4 galacturonosyl linkages; however, these natural link are often interrupted by L-rhamnose units bearing side-chains, which causes a discontinuity in the linear conformation of the poly-(GalA) chain. Some of the carboxyl group on the continuous poly-(GalA) chain of pectin are esterified by methyl groups informing variation in the degree of methyl esterification (DE or DM). This results in its classification as high methoxyl (HM) and low methoxyl (LM) pectins, depending on whether DE is greater or less than 50%, respectively (WHO/FAO, 1981). Homogalacturonans (HG), rhamnogalacturonan-I (RG-I), and substituted galacturonans (SG or RG-II) are the three main structural classes of pectin (Ridley, O'Neill, & Mohnen, 2001). The biosynthesis of pectin is also known to be complex and its understanding is currently characterized by much speculation (Caffall & Mohnen, 2009; Ridley et al., 2001).

Such diverse microstructural and macromolecular properties of pectin form the basis for its various food and non-food applications, which includes their reported health-promoting benefits and bioactivities (Endress, 2011; Yamada, Kiyohara, & Matsumoto, 2003).

For example, pectins with low-molecular weight and chemically modified structures are said to instil satiety-inducing effects, selective cytotoxicity leading to anti-colon cancer activities, enhancement of cardiovascular health, and insulin and gastric inhibitory polypeptides (GIP) reduction (Almeida et al., 2015; Brown, Rosner, Willett, & Sacks, 1999; Hasselwander, 2008; Maxwell, Belshaw, Waldron, & Morris, 2012; Rabbani et al., 2001, 2004). Texturizing applications of pectin in food and similar systems, including gelling, viscosity enhancement, and colloid stabilizing, are fundamentally related to its in-solution (gels or dispersions) behaviour, the basis of which have been previously discussed (Lopes da Silva and Rao, 2006). Food sectors like dairy, bakery, and nutraceutical and functional foods (Anton & Artfield, 2008; Bierhalz, da Silva & Kieckbusch, 2012; Burnside, 2014; Li & Nie, 2016; Phillips & Williams, 2009; Rababah, Al-u'datt, & Brewer, 2015; Ramaswamy & Basak, 1992; Schmidt et al., 2015; Tromp, de Kruij, van Eijk, & Rolin, 2004; Zhuang, Sterr, Kulozik, & Gebhardt, 2015) as well as pharmaceutical domains like drug delivery (Liu, Fishman, & Hicks, 2007), exploit pectin. The book chapter by Endress (2011) provides a great overview of the basis of its current as well as prospective functionalization for nutritive and texturizing purposes.

Utilizing pectin, however, begins with its isolation from the parent plant material. This entire pectin production process is well documented in literature and is summarised in Fig. 1; it broadly includes a raw material pre-treatment stage, an extraction operation, and a post-extraction stage (Gentilini et al., 2014; Kai, Yan, Sijin, Xiaojun, & Xiaosong, 2008; Kratchanova, Panchev, Pavlova, & Shtereva, 1994; Lopes da Silva & Rao, 2006; May, 1990). However, one of the questions raised regarding the conventional pectin production process, particularly the extraction step, is whether or not the valorisation of fruit and vegetable processing by-products is really worth energy and economic demands that are currently associated with the practice (Casas-Orozco, Villa, Bustamante, & González, 2015). Besides this resource conservationist's viewpoints, the extended heating duration required, also raises the question of whether the process duration can be reduced, thereby resulting in better quality and with somewhat consistent physicochemical properties of pectin. To this end, several sustainable and quicker alternative approaches to extracting natural compounds from biological materials have emerged. Some prominent outcomes of adopting these novel methods include shorter extraction

Table 1
Comparison of some commercial and non-commercial sources of pectin.

Source/utilized segment	Content (% dry wt)	Probable natural class of pectin ^a	References
<i>Conventional</i>			
Citrus peel	30–35	HM	Lopes da Silva and Rao (2006)
Apple pomace	15–20	HM	Lopes da Silva and Rao (2006)
Sugar beet pulp (post-sugar extraction)	15–30	HM	Michel, Thibault, Mercier, Heitz, and Pouillaude (1985); Peng et al. (2015)
Sunflower seed head	5–25	LM	Miyamoto and Chang (1992); Wiesenborn et al. (1999)
<i>Unconventional</i>			
Cranberry, onion, garlic, banana, mango, pumpkin, peach, rapeseed, papaya	0.1–28	LM and HM	Alexander and Sulebele (1973); Jeong et al. (2014); Kalapathy and Proctor (2001); Maran and Prakash (2015); Pagán, Ibarz, Llorca, Pagán, and Barbosa-Cánovas (2001)

^a LM – low methoxyl; HM – high methoxyl.

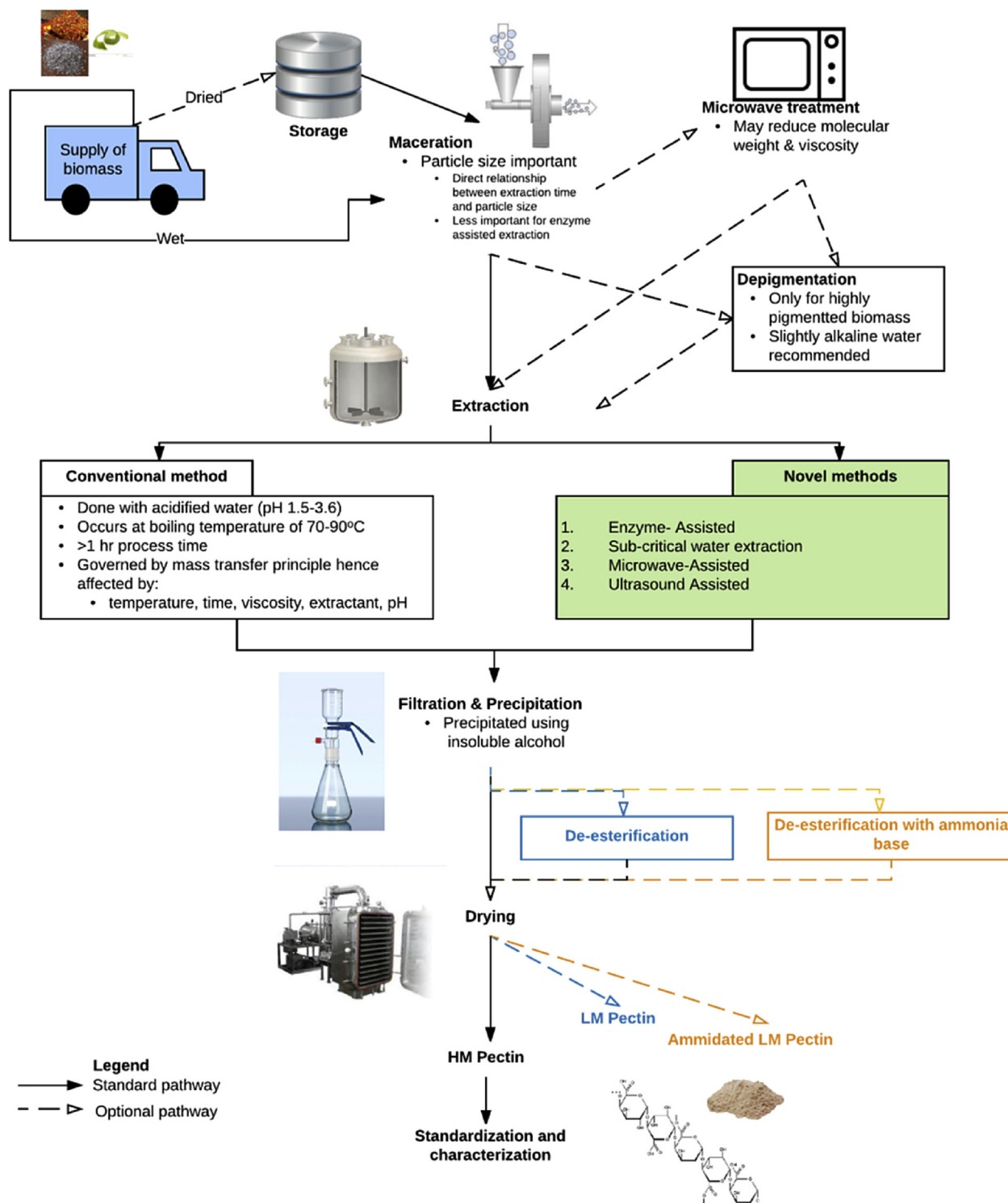


Fig. 1. The industrial pectin production process.

time, reduced temperature, increased yield and/or lower solvent consumption, and even delivered superior quality extracts than conventional methods. The most promising of these innovative extraction techniques relevant to pectin extraction include enzyme-assisted extraction, ultrasounds, use of subcritical fluids, pulsed electric field extraction, high hydrostatic pressure and microwave heating, hence, their increasing examination.

So this review aims to assess these novel extraction techniques

and how they influence the mass transfer of pectin from various plant-based raw materials. The chances and odds of a mainstream industrial integration of these non-conventional extraction methods is undertaken.

2. Novel techniques for pectin extraction

Extraction processes are governed by mass transfer principles

and so isolating pectin is a function of how fast: (a) the hydrolysis of the protopectin (i.e., the *in situ* pectic polysaccharide, bound to other cell wall compounds like cellulose) from the raw material occurs; (b) the resultant pectin gets solubilized; and (c) the extraction solvent attains a state of equilibrium (or saturation) (Minkov, Minchev, & Paev, 1996; Pinelo, Sineiro, & Núñez, 2006). Hence, it is generally agreed that the extraction process follows two real-time events of *hydrolysis* and *solubilisation* (Cho & Hwang, 2000; Minkov et al., 1996), where the latter includes the outward diffusion of dissolved pectin into the bulk solvent. Mathematical models that integrate both the hydrolysis and the dissolution-cum-degradation have been developed to follow a first-order chemical reaction (Cho & Hwang, 2000; Minkov et al., 1996). One of these models was used to quantify the rate of degradation of pectin, as exemplified in molecular weight and intrinsic viscosity of the extracted pectin (Cho & Hwang, 2000). Protopectin hydrolysis for a given spherical pectin-bearing particle has been shown to follow the relation:

$$\frac{dC}{dt} = -kC(1 - \varepsilon) \quad (1)$$

where, C is the protopectin concentration, k is the rate constant of hydrolysis, ε is the porosity of the particle (Minkov et al., 1996). Although hydrolysis of the insoluble protopectin from other cell wall polysaccharides is integral to the successful extraction of pectin from plants, improper control of relevant factors—chiefly temperature and solvent pH—will yield pectin having inferior physicochemical properties.

On the other hand, the rate-limiting step in which dissolved pectin is diffused through the pores of the solid particle to its surface has been described, with factors such as temperature and solid-liquid ratio considered important. In an extraction process temperature has been reported to influence diffusivity, D , according to the Stokes-Einstein relation:

$$D \propto \left(\frac{T}{\eta} \right) \quad (2)$$

where T , is the absolute temperature and η , is the dynamic viscosity coefficient (Loncin & Merson, 1979).

Factors to consider to obtain quantitative and qualitative extract during pectin extraction can be broadly viewed as: technology-related issues (which includes optimal operating conditions, among them, temperature and pressure), intrinsic factors based on biomass/matrix pre-treatment condition (like particle size and moisture content) and extrinsic factors based on the solvent (like polarity, volatility, molecular weight, solid-liquid ratio, and even toxicity of the solvent used). Study of the influence of these factors on pectin extraction has previously been undertaken by El-Nawawi and Shehata (1987).

In spite of an enhanced extraction efficiency (yield per unit time) at high operating temperatures, the somewhat heat-labile nature of pectin restricts the extent to which the temperature can be raised. This is because, at such temperatures, excessive depolymerisation and de-esterification of the protopectin can occur, yielding extract with poor functional properties, thus limited industrial use (Lopes da Silva and Rao, 2006). Equation (2) also demonstrates the reliance of diffusivity on viscosity; this is related to the increasing concentration of the extract-containing solution as extraction progresses.

The mass transfer rate also decreases with time due to a declining concentration gradient. More so, as the concentration of pectin in the extraction solvent increases, the solution tends to become more viscous, contributing to the said mass transfer rate

decline (Richardson, Harker, & Backhurst, 2002). The implication of this is that there is an optimal duration for the extraction of pectin, beyond which the pectin dissolution not only ceases, but thermal degradation of the polysaccharide heightens.

The ratio between solid material to extractant, known as liquid-solid (L/S) or solid-liquid ratio (S/L), is also considered important and should be optimized. For most investigations, S/L is typically represented in units of mass per volume (e.g. g/ml). Increasing the solvent percentage was shown to favour concentration gradient while decreasing the viscosity of the solution; this results in higher extraction rate and yield. Nonetheless, excessive L/S is detrimental for two reasons, namely: (i) economics dictate less (or optimized) use of solvent, which would otherwise mean higher energy and wastewater disposal costs; and (ii) hydrolysis of the extracted pectin results from over-dilution of the solution (Kertesz, 1951). Kulkarni and Vijayanand (2010) extracted pectin from passion fruit peel using an aqueous hydrochloric acid (50% wt) as solvent, and varied the solid to liquid ratio between 1:10 and 1:40 (w/v). The authors reported that yield was significantly higher at a ratio of 1:30 than in 1:10; however, further increase in solvent volume did not have significant effect. Hence, it was concluded that a solid/liquid ratio of 1:30 (w/v) was sufficient to give a high yield.

The pH of the extraction solvent is a most sensitive factor to note while extracting pectin. Generally, low acidic pH is necessary for the hydrolysis of the protopectin; although alkaline treatment are also useable, these are unsuitable because of increased pectin degradation at neutral and high pH conditions by β -eliminations (Kravtchenko, Arnould, Voragen, & Pilnik, 1992). A trade-off is often made between having a better quality but low yield at high pH and having a poor quality extract but with higher yield at a lower pH; this compromise is made holistically with temperature and extraction time. Typically-reported values for pH range between 1 and 3 (Jensen, Sørensen, and Rolin, 2013; Lopes da Silva and Rao, 2006). Along with the acid used, the pH of the mixture can be adjusted using minor amount of a suitable base (e.g. NaOH).

As previously mentioned, particle size of raw material, together with particle size distribution (PSD), is a critical factors in pectin extraction. El-Nawawi and Shehata (1987) demonstrated that higher yields were obtained at smaller particle sizes. This is collectively due to increased surface area of contact between solid and solvent and smaller diffusion distance for the solute. But with particle size that is too fine, there is a challenge of some impedance to solvent flow through material. In addition, a small range of particle sizes is advocated, since a large PSD means that the finer particles may be jammed within the crevices of adjoining coarser ones, thereby hindering solvent flow (Richardson et al., 2002). One technical factor that El-Nawawi and Shehata (1987) assessed, which did not significantly influence extraction yield of pectin, was the agitation of the solvent. The authors alluded this to the two outward diffusion processes; one is the transport of the solute within the solid matrix, which is a more rate-limiting step than the second, which is the diffusion of solute from matrix surface to the bulk solvent. Had the reverse been the case, the eddy diffusion induced by agitation would have enhanced extraction yield.

It was mentioned earlier that a number of non-conventional techniques have been explored with a view of replacing the conventional extraction approach and ameliorating the pectin production process; these have been used to obtain qualitatively and quantitatively better extract in a less energy-intensive duration. The methods used for pectin extraction can be broadly grouped into chemical, physical, and enzymatic extraction processes. To replace such established practice, scalability is always a factor, hence only the potentially scalable methods pertinent to pectin extraction are described below.

2.1. Enzyme-assisted extraction (EAE)

2.1.1. Underlying principles and mechanisms

One method touted as the potential panacea for unintended but unavoidable presence of trace chemical solvents in products from solvent-based extraction processes, among other merits, is enzyme-assisted extraction (or EAE) (Puri et al., 2012). With the increasing pressure on food and pharmaceutical industries to develop sustainable chemical processes (including extraction), it has become imperative to seek alternative solvent-conservative approaches such as this for these processes. Enzymes are commonplace in juice processing for clarifying. Additionally, Rhein-Knudsen, Ale, and Meyer (2015) reviewed EAE of seaweed hydrocolloids—carrageenan, alginate and agar—highlighting the various effects that such process has on the physicochemical properties of the marine polysaccharides.

Chiefly owing to their mode of operation, enzymes are able to catalyse reactions such as hydrolysis, with a high level of selectivity which either reduces the amount of solvent/chemical needed or increase yield for the same amount of solvent (Puri et al., 2012), in a way that is not feasible with acid-based hydrolysis. The plant cell wall is composed of an entangled network of polysaccharides—including cellulose, hemicellulose (like xyloglucan), and pectin—and protein, with demonstrated interactions between them; the cellulose/xyloglucan network is implanted in a matrix of pectin along with a protein network (Fissore et al., 2009; Panouillé, Thibault, & Bonnin, 2006). Selective cell wall component-degrading enzymes such as cellulases, hemicellulases and proteases with minimal pectinolytic activity are often used to effect hydrolytic actions in the respective non-pectin plant cell wall components, but this requires a good knowledge both of the catalytic action of the selected enzyme/s and the optimum conditions for their use in EAE (Ptichkina, Markina, & Rumyantseva, 2008; Puri et al., 2012).

A distinction is possible between two approaches of EAE of pectin, namely: (i) using enzymes that degrade pectin and help isolate pectin fragments e.g. galacturonic acid, and (ii) using enzymes capable of deconstructing plant cell wall and isolating pectin (Panouillé et al., 2006). While the latter approach is common, examples of the former are also seen in the works by Zhao et al. (2015), who studied de-esterification of commercial HM pectin

into LM using a synergistic application of high hydrostatic pressure (HHP) and pectin methyl esterase (PME) enzyme, and Zykwiniska et al. (2008) who demonstrated that a direct incorporation of PME alongside cellulases and proteases into the EAE process resulted in LM pectin from an otherwise HM pectin source.

2.1.2. Operational issues for enzyme-assisted extraction

Operating EAE would typically require some level of size reduction of the pectin-bearing substrate for improved access to the cells, and like most other extraction techniques, enzymes can be selected for targeted functionalities and for optimum process conditions (Puri et al., 2012). Process conditions of particular interest in EAE processes include temperature, enzyme composition and concentration, hydrolysis time, pH and solvent ionic strength, solvent-biomass ratio, and, to a lesser extent, moisture content of substrate.

As shown in Table 2, several studies exist attempting to optimize the EAE process with some interesting and sometimes conflicting results. Ptichkina et al. (2008) studied the EAE of pectin from grey pumpkin (*Cucurbita pepo*). Preliminary evaluation of the catalytic activity (viz, cellulase and pectinase) of a number of commercial enzymes was done, with *Aspergillus awamori* giving the best result; conditions included a constant at 3 h hydrolysing time and enzyme concentration was 1% (w/v). Compared to yield from the same substrate but with different enzyme (*Bacillus polymyxa*) obtained by other researchers (Matora et al., 1995). The authors reported lower yields (14% vs 22%) albeit for lower extraction time of 3 h (compared to 24 h). It was hypothesized that the presence of pectin esterase in this enzyme could be useful in producing pectins with variable degrees of esterification. Jeong et al. (2014) employed different mixing proportions of two commercial enzymes (Celluclast® 1.5L and Alcalase®) in the EAE of pectin from defatted rapeseed cake. A combination of 1:4 Celluclast-Alcalase ratio gave the best yield (6.85%) at constant pH and temperature conditions. However, in such a way, a LM pectin with DE<50% was obtained. This shows the possible benefits of synergistically applying different enzymes.

Contrasts have been drawn between EAE and conventional heating extraction (CHE) method. Wikiera, Mika, and Grabacka (2015) compared EAE and conventional acid extraction of apple

Table 2
Effects of enzymatic activities on pectin and pectic oligosaccharides recovered from plant materials.

Biomass	Enzymatic treatment			Other conditions	Catalytic effect on extract	Reference
	Class	Concentration a/activity	Time, h			
Chicory roots	Protease Cellulose Pectinase	1:10 (v/v)	8–48	T, 40 °C (then 100 °C post-EAE); solvent, sodium acetate.	~25% higher yield increase over CHE; lower MW	Panouillé et al. (2006)
Cocktail of sundry crops (chicory, citrus, cauliflower, endive, sugar beet)	Cellulase Protease Pectin methyl esterase	1/10 (v/v)	4	T, 50 °C; mixing rate, 120 rpm; S/L, 1/100 and 1/50 (w/v); solvent ionic strength, 0.05 M sodium acetate buffer.	Healthful oligosaccharides are obtainable after EAE of pectin; HM pectin; LM pectin obtainable by addition of commercial pectin methyl esterase enzymes	Zykwiniska et al. (2008)
Butternut (<i>Cucurbita moshata</i>)	Cellulase Hemicellulase	1:200 and 1:40 (w/w), respectively	20	T, 30 °C; S/L, 1/100 (w/v); solvent ionic strength, 0.05 M sodium citrate buffer.	~30% higher yield by hemicellulase; Higher DE (72.6 vs 54.2) and rheology by hemicellulase-based EAE	Fissore et al. (2009)
Lime peel	Cellulase Hemicellulase (including xylanase, arabinoxylanase)	1/533 (v/v)	4	T, 50 °C; pH, 3.5; S/L, ~1/30 (w/v); solvent ionic strength, 0.05 M citric acid buffer.	Tweaking pH can allow EAE pectin with consistently high yield, and homogeneous/ repeatable quality	Dominiak et al. (2014)
Lime peel	Cellulase Xylanase	0–50 U/g	0.5 + 3.5 ^b	T, 50 °C; pH, 4.5; P, 100 MPa; S/L, 1/ 30; solvent ionic strength, 0.05 M citrate buffer.	30 min pressure improved yield; xylanase significantly affected yield, GalA and DE	Naghshineh, Olsen, and Georgiou (2013)

^a Units used for concentration varied among studies; w/w is relative to biomass, while v/v relative to solvent.

^b a combination of 30 min high pressure processing and then 3.5 h of EAE—both at 50 °C.

pomace pectin. The authors reported that pectin obtained by EAE (using Celluclast®) had higher molecular weight (490.30 vs 192.73 kDa) than conventionally isolated ones, even though their galacturonic acid contents (56.56 vs 56.44%) were not significantly different. In an earlier comparative study of EAE and CHE of pectin from chicory and cauliflower, commercial cellulases (Celluclast®) and proteases (Neutrase®) were used in the EAE, and, again, extraction yield was higher (34.6%) compared to CHE (27.8%) (Panouillé et al., 2006). However, a lower molecular weight was reported for pectin from EAE as compared to that from CHE (~300 kDa and 500 kDa, respectively), and this was vaguely ascribed to the enzymatic extraction mechanism.

2.1.3. Benefits and drawbacks of enzyme-assisted extraction

From these reviewed studies involving the use of enzymes in pectin recovery, one sees a number of benefits of the method. As mentioned earlier, the need for acidic pH levels and high temperature can be eliminated using EAE. Wastewaters possessing these extreme properties are consequent of the current industrial practice, but using these site-specific enzymes and generally low-temperature solvents can slow down equipment corrosion. Moreover, it is a regulatory requirement to neutralize the large volume of sewage from the conventional method, which can both be reduced and the burden eased with the adoption of an enzyme-assisted process. Another advantage of this green extraction method is the reduced need for certain pre-treatment steps (e.g., excessive size reduction of the raw material and washing off sugars and colour pigments) as is the case with conventional and physical techniques (Wikiera et al., 2015). The result is a marked decrease in overall extraction time and a faster extraction process. This probably occurs due to enhanced desorption process observed in the pectin material through enzymatic hydrolysis.

Further, enzyme activity means that solvent pre-treatment of the pectin-containing material has more effect than without the action of enzymes, resulting in higher extraction yield and/or reduced solvent requirement (Puri et al., 2012). Reduced solvent use is particularly desirable especially in the face of current move to adopt “green” chemistry. Moreover, less extraction solvent means less volume of alcohol needed for extract precipitation, which translates to significant cost savings for industry in the long run. Also, with adequate articulation of factors and giving the mild conditions associated with this process, it is possible to obtain improved quality of pectin extract—in terms of degree of esterification and molecular weight—by using EAE over other solvent extraction techniques (Ptchikina et al., 2008; Sowbhagya & Chitra, 2010). Perhaps, the most plausible benefit of using this green technique for the extraction of pectin, as Rhein-Knudsen et al. (2015) pointed out for seaweed hydrocolloids (agar, alginate and carrageenan), will be that the structural traits and functional

properties of the target polysaccharides are preserved.

While these advantages of enzyme-assisted extraction exist, translation of this promising technique beyond laboratory scale into mainstream industrial use is currently pegged back by a number of factors. First is the cost of enzymes. Extracting pectin enzymatically in the lab scale would require relatively low concentrations. However, on the industrial scale where large volumes of raw materials are handled, their cost take another dimension making the route more expensive and less attractive to industry. For similar reasons, scale-up of EAE process can be difficult because of the uniqueness in response of different enzymes to changing environmental conditions such as temperature and nutrient availability which in turn influences pectin yield; these conditions are properly monitored in the lab, but may be not quite so in a big plant, where they can change really fast and often uncontrollably (Puri et al., 2012)—indeed, this dilemma in process control towards seamless scale-up is one that constrains many food industry processes (Norton, Fryer, & Moore, 2006). In addition, EAE does not necessarily shorten extraction time, a critical criteria for judging a technique's suitability to displacing CHE. For these reasons, EAE of pectin is still a talk widely limited to academia and research circles, and the wait is on to see how the subject of scalability is resolved in the future.

2.2. Subcritical water extraction (SWE)

2.2.1. Underlying principles and mechanisms

Subcritical water is liquid water at elevated pressure which is able to attain temperatures higher than its normal boiling point without a change of phase. When such water is used as solvent in extraction, the process is known as subcritical water extraction (SWE)—also known as pressurized hot water extraction (PHWE) and superheated water extraction (SHWE) (Zakaria & Kamal, 2015). In cases where a subcritical solvent other than water is used, the process is known as accelerated solvent extraction (ASE); hence, many studies that apply this principle for extraction within the food and environmental domains may report it in different names (Hawthorne, Grabanski, Martin, & Miller, 2000; Ibañez et al., 2003). The elevated temperature of water results in a number of physical advantages such as high diffusion, low viscosity, low surface tension, increased vapour pressures, and higher mass transfer rate. Furthermore, physicochemical property of subcritical water—including dielectric and solubility—are significantly altered at such conditions (Azmir et al., 2013; Zakaria & Kamal, 2015). Dielectric constant of water is around 79 at 25 °C but this reduces to 43 at 160 °C, and to 33 at temperatures around 200 °C, making it possible to extract both ionic and non-ionic compounds (Brunner, 2009; Chen, Fu, & Luo, 2015; Ueno, Tanaka, Hosino, Sasaki, & Goto, 2008). Fig. 2 shows the typical SWE scheme as used in

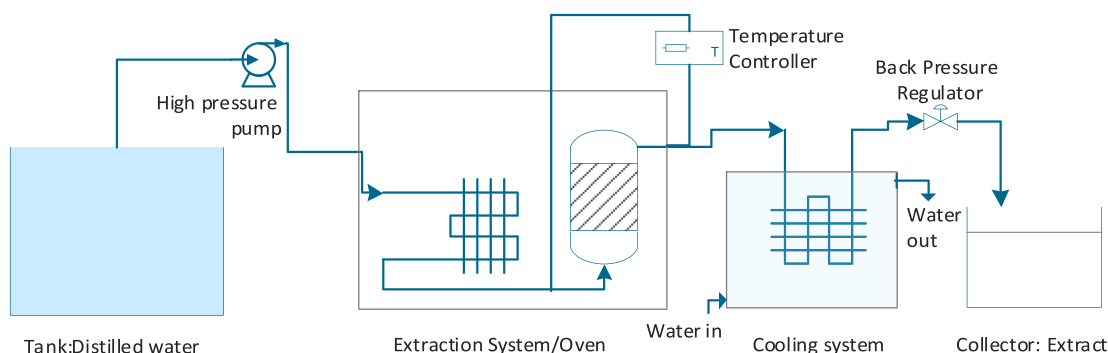


Fig. 2. Basic scheme for the subcritical water extraction [adapted from Ueno et al. (2008) and Zakaria and Kamal (2015)].

pectin recovery.

2.2.2. Operational issues for subcritical water extraction

Similarly, the solubility parameter of water can also be improved at subcritical conditions (Zakaria & Kamal, 2015). For example, the Hansen solubility parameter (HSP) has been used to optimize the extraction condition by Srinivas, King, Monrad, Howard, and Hansen (2009). The authors tested the applicability of the prediction tool on SWE of three bioactive compounds, namely: botulin from birch bark, niacin from spent brewer's yeast, and flavonoids from grape pomace, and could be adapted for pectin extraction prediction. The tool can be used to estimate the conditions for solute-solvent miscibility, an optimum temperature range for conducting extraction under pressured conditions, and approximate/suitable extraction conditions for particular solutes from natural matrices (Srinivas et al., 2009). These property transformations resulting from change in temperature condition can result in an improved extraction rate. In pectin extraction, temperatures as high as 170 °C have been investigated. Although the primary role of pressure is to keep the water from boiling into the vapour phase (Zakaria & Kamal, 2015), this property also influences the yield of pectin as demonstrated by Chen et al. (2015) and some studies have investigated SWE at pressures up to 10 MPa. Furthermore, extraction time remains a key factor in SWE of pectin as an excessively long extraction period could result in degradation; hence, time should also be considered during the process of optimization. Particle size of the biomass could also play a role during SWE, especially with regards to pectin yield.

This technique can potentially transform the pectin extraction process from batch to a continuous or semi-continuous one, and this is because the subcritical water in an SWE system has a flow rate. Flowrates ranging from 2.1 to 7.0 ml/min were tested in an SWE module, and it was found that lower pressure in the vessel resulted in a haphazard flow regime (Ueno et al., 2008). However, batch operation of SWE of pectin is also employed, in which case the *S/L ratio* becomes a pertinent factor (Wang, Chen, & Lü, 2014).

Recently, a few studies have started developing SWE processes for pectin from various plant matrices. Ueno et al. (2008) compared SWE to the conventional hot hydrochloric acid extraction to obtain pectin from the flavedo of Citrus junos. Authors found that the extraction rate increased rapidly at subcritical water temperature 160 °C, explaining that the high temperature, leading to lower dielectric constant of the solvent, was responsible for the improved solubility of pectin in water.

In another work, pectin-enriched materials from sugar beet pulp was extracted using a synergistic application of ultrasound-assisted treatment and SWE (Chen et al., 2015). As against the commonly reported trend of lower yield at temperature above 80 °C, which is attributed to the degradation of pectin at such temperature, the method used by Chen et al. (2015) gave increasing yield until a temperature of 120 °C which means that subcritical water can help avoid the acid hydrolysis found in conventional acid extraction, while increasing mass transfer and optimum extraction temperature. However, as temperature approached 160 °C, a gradual decrease in yield was observed owing to lower density and, by extension, smaller solute-carrying capacity of water. Similarly, an optimum value was reported for extraction time (30 min) up to which yield increased but beyond which yield decreased significantly. This was attributed to the probable thermal degradation of pectin which may begin after the time needed for its complete dissolution in the solvent has been exceeded. Citrus peel and apple pomace pectins were extracted using SWE (Wang et al., 2014). It was, again, reported that there was an optimum level of temperature required for the extraction process. Pectin from citrus gave a maximum yield of 21.95% at 120 °C, while apple pectin yielded a

maximum of 16.68% at 150 °C.

2.2.3. Benefits and drawbacks of subcritical water extraction

A case can be made for the benefits offered by this environmentally benign SWE process. Higher quality extracts, quicker extraction process, and savings in (or elimination of) acidic co-solvent utilization, are a few of them (Ueno et al., 2008; Zakaria & Kamal, 2015). More so, use of a solvent that is generally recognized as safe (GRAS) makes this technique suitable for food and pharmaceutical compounds like pectin.

Improper control of process conditions can however result in hydrolysis of the pectin chain which can be problematic if such degradation is not the goal, as in pectin extraction (Khajavi, Kimura, Oomori, Matsuno, & Adachi, 2005). Additionally, the cost of implementing might also be considered a put-off for this technique in the pectin production industry.

2.3. Microwave-assisted extraction (MAE)

2.3.1. Underlying principles and mechanisms

Microwave (MW) is an electromagnetic wave consisting of two oscillating perpendicular fields: electric and magnetic fields. MWs range in frequency between 300 MHz and 300 GHz on the electromagnetic spectrum. MWs are often used as information carriers or as energy vectors with the latter application commercially utilizing mostly frequency bands at 0.915 and 2.450 GHz; most home microwave ovens operate at 2.450 GHz (wavelength, 12.2 cm; energy 0.94 J/mol) (Letellier & Budzinski, 1999; Venkatesh & Raghavan, 2004; Voss, 1974). Such frequency causes a disorganized rotation of the polar molecules of a MW-irradiated matrix and/or solvent which in turn creates heat. However, heat is only generated if the material has dielectric losses, that is, if it absorbs some of the energy. Hence, the absorbed energy is obtained from the expression for dissipation factor (δ):

$$\tan \delta = \epsilon'' / \epsilon' \quad (3)$$

where ϵ'' and ϵ' are the real (dielectric constant) and complex (dielectric loss factor) part of dielectric permittivity, ($\epsilon^* = \epsilon' - j\epsilon''$), respectively (Venkatesh & Raghavan, 2004). Whereas ϵ' expresses the ability of an irradiated molecule to become polarized by the electric field, ϵ'' is an indication of the efficiency of transformation of electromagnetic energy into heat (Letellier & Budzinski, 1999). One advantage of this form of heating is the homogeneous temperature distribution in the medium whereby, as Venkatesh and Raghavan (2004) noted, there is no temperature gradient as is the case with conventional thermal processing.

In microwave heating, the transfer of energy follows two mechanisms: dipole rotation, involving the reversal of dipoles in polar molecules; and ionic conduction, involving displacement of charged ions present in the solvent (Routray & Orsat, 2012).

2.3.2. Operational issues for microwave-assisted extraction

In MAE of pectin, the choice of solvent is an important factor, both in terms of nature (pH) and volume. Other integral factors that are considered as related to microwaves include the choice of microwave system, the MW power density and the operating conditions like temperature. These conditions form the basis for MAE of pectin studies (Table 3) and are discussed in the following section. The characteristics (i.e., moisture content and particle size) of the plant matrix to be extracted are also considered during microwave-based extractions.

Instrumentation for analytical studies involving pectin extraction by MW often consists of either of two systems of commercially

Table 3

The effects of microwave heating on pectin extraction.

Plant tissue	MW conditions				Effects of MW on yield and quality	Reference
	Power, W	T, °C	t, min	S/L, g/ml		
Lime	630	140	3.00	1/25	High M_w (310–515 kDa); M_w , $[\eta]$, radius of gyration (R_g) decreased with heating time.	Fishman et al. (2006)
Citrus reticulata	422	NS ^a	2.82	1/16.9	Yield increased with MW power but decreased with pH, time and S/L	Prakash Maran et al. (2013)
Apple	499.4	NS	20.80	1/14.5	MAE significantly lowered extraction time	Wang et al. (2007)
Dragon fruit	400	45	20.00	1/24	Threshold values for MW power and temp were identified for optimized extraction.	Thirugnanasambandham et al. (2014)
Sugar beet	1200	60	3.00	1/25	High M_w (~1.2 million Da) and moderate-viscosity (~4.3 dL/g) pectin recovered	Fishman et al. (2008)
Mango	413	NS	2.23	1/18	All factors considered influenced yield significantly.	Prakash Maran et al. (2015)
Carica papaya	514	NS	2.33	1/15	Factors strongly imparted yield	

^a Not stated.

available microwave ovens or cavities. Although further classifications can be made based on other metrics, monomode (or focused) microwave ovens and multimode (or closed) microwave oven distinguish different microwave systems (Letellier & Budzinski, 1999). Another nuance within this classification involves the level of process condition (pressure and temperature) control within the oven. Fishman, Chau, Cooke, and Hotchkiss (2008) reported using a temperature- and pressure-regulated closed microwave oven for pectin extraction from sugar beet. Their data showed that requisite process conditions (T, 60 °C and P, 30 lb/in²) were attained in a little over one minute. Conversely, the focused system requires that the irradiated sample be exposed to atmospheric pressure. Accordingly, the system is considered safer, since improper control of pressure in the closed system can be dangerous for both user and equipment (Leonelli, Veronesi, & Cravotto, 2013). A number of recent studies have used both of these MW systems for the extraction of pectin from biomass with varying results, but the multimode/oven configuration is more commonly studied.

Successful use of microwave-assisted extraction (MAE) of pectin depends on the dielectric properties of the solvent, in this case acidified water. But in addition to the solvent properties (i.e., nature and volume) consideration should also be given to the microwave power (or energy density), temperature and matrix moisture content. Water is a major absorber of microwave energy in food and biological materials, hence, the higher the moisture content of the bio-material, the more rapid is its response to microwave heating (Venkatesh & Raghavan, 2004). In the use of microwave energy, two principles of extraction exist (Letellier & Budzinski, 1999), namely: (i) Direct heating of target of the microwave-absorbing matrix, leading to a release of target compound into an otherwise cool solvent; or (ii) Heating of a polar solvent to boiling point, leading to the extraction of the compound. In the first case, solvent acts to solubilise the extract and cool the matrix. The second pathway is more applicable to pectin extraction, since water (a polar solvent with rapid dipole rotation) and acid (having two oppositely-charged ions—like H⁺ and Cl[−] in the case of HCl—with high ionic conductivity) used combine to give a solvent having a high dielectric loss (Fishman, Chau, Hoagland, & Hotchkiss, 2006). Thus, increased microwave power can raise temperature within the system and lead to increase in pectin yield has been repeatedly reported (Prakash Maran, Sivakumar, Thirugnanasambandham, & Sridhar, 2013; Wang et al., 2007). But as is the case with CHE, at an observable threshold, further increase in MW power (by extension, temperature) causes a decline in yield owing to the rather thermolabile nature of pectin. This latter effect was also reported for MAE of flavonoids (Routray & Orsat, 2012). The reasons for the initial increase in extraction efficiency can be linked to the lower viscosity and surface tension, which expedites hydrolysis and

solubility of protopectin and pectin, respectively. This fact holds true especially in closed MW systems, where temperatures can be higher than the boiling point of water; Fishman et al. (2006) reported temperature values of about 140 °C. It is, therefore, important to select an optimum MW power such that the time required to attain the set temperature is minimized; even at low temperature, an ill-selected power and the resultant extension in “heat-up” time can, and has been found to, lower yield of extract due to degradation.

Perhaps the most influential factor on the yield and quality of pectin is the time of exposure to the MW power, also known as irradiation time. Generally speaking, when irradiation time increases, there is an initial increase in yield, but like temperature, declining yield have been observed beyond some duration. Hence, in MAE process optimization, the duration of MW exposure should be considered. Prakash Maran, Swathi, Jeevitha, Jayalakshmi, and Ashvini (2015) optimized an MAE process of pectin from waste mango peel using response surface methodology (RSM). Time, one of four factors examined, was shown to favour pectin yield up until 2 min after which yield dropped. As noted earlier, the solvent system (acid-water) mostly used for pectin extraction are well suited to microwave heating, reaching high temperatures in short time; however, extended exposure to such high temperatures will result in depolymerisation/degradation of the hydrolysed pectin, yielding polymers with low degree of polymerisation that do not precipitate in alcohol, hence the reported decline in extract.

Longer extraction times have been reported though, and the only rational conclusion will be the variation of MW resistance among feedstocks. Wang et al. (2007) performed MAE of apple pomace pectin, varying extraction time between 10.6 and 17.4 min but found the optimal extraction time to be around 20.8 min using RSM. In the range studied, the authors observed no decline in yield with increasing time, which was considered quicker than the conventional method of extraction. It is thus seen that “short time” used in this case is relative, since if used for extracting mango peels could result in poorer yields. Dragon fruit pectin extraction was also reported to require such duration of MW exposure (Thirugnanasambandham, Sivakumar, & Prakash Maran, 2014).

The role of solvent choice for MAE processes has been highlighted by Veggi, Martinez, and Meireles (2013) and would not be discussed here; moreover, the question of what solvent to use for pectin extraction has long been answered. Hence, it is commonplace in pectin MW-assisted extraction research to focus on the optimal ratio of solid-solvent ratio (S/L) instead. While MAE has been reported as significantly lowering solvent use, solid-liquid ratio remains an important factor that should be optimized in any MAE process, especially for extracts that form colloids in the solvent, as with the hydrocolloid pectin. This is because the solution

can attain equilibrium/saturation level and become too viscous. Wang et al. (2007) extracted pectin from apple using MAE and observed a technical difficulty during the filtration of extracted pectin for systems containing solvents less than 14.49 ml per gram of biomass.

The effect of MAE, and another technique (ultrasound assisted extraction), on qualitative and quantitative characteristics of extracted grapefruit pectin was assessed (Bagherian, Zokaee Ashtiani, Fouladitajar, & Mohtashamy, 2011). Results indicated that not only do yields increase with increasing microwave power (0.45, 0.63, and 0.9 kW), but also yields were generally higher (21.23, 22.71, and 26.27%) than in conventional acid extraction (19.16%). Similarly, values for DE increased generally with increasing microwave power and time (70.96–80.89%). Galacturonic acid unit contents were also found to be higher with increasing power and time.

In the optimization of pectin (apple pomace) extraction process using MAE, Wang et al. (2007) found the highest yield (0.315 g/2 g dried apple pomace) at optimum conditions: time, 20.8 min; solid-liquid ratio, 0.069; pH, 1.01; microwave power, 499.4 W. This time is comparatively lower than those reported for conventional heating (Cho & Hwang, 2000; Minkov et al., 1996).

2.3.3. Benefits and drawbacks of microwave-assisted extraction

Two obvious advantages of MAE are the reduced extraction time and lower solvent requirement. But certain underlying factors which are responsible for these two advantages can also be considered as merits as has been established in other microwave uses within the food industry. First, the non-conventional heating principle in MAE means there is a homogeneous temperature distribution within the medium with no temperature gradient. Also, equipment size can be considerably reduced. Qualitative and quantitative characteristics of MW-extracted pectin have shown improvements over conventional extraction techniques (Bagherian et al., 2011; Fishman, Chau, Hoagland, & Ayyad, 1999). Hence, the MAE technology is a recognized green technology.

In spite of the reduced volume of acidified water used in an MAE process (these lower ratios have more economic saving connotations), the mere fact that such acid solvent is used, and must be discarded, still brings about the corrosion problem and subsequent wear of equipment.

2.4. Ultrasound-assisted extraction (UAE)

2.4.1. Underlying principles and mechanisms

Sound waves with frequencies from 20 kHz (above the audible range of the human ears: 1–16 kHz) are referred to as ultrasound. These waves differ from electromagnetic waves in that, a medium (solid, liquid or gas) is required for their propagation, involving a series of expansion (which pulls molecules apart) and compression cycles (which pushes them together). For a liquid medium, the expansion cycle can create bubbles/cavities which grow and subsequently experience collapse as the negative pressure exerted exceeds the local tensile strength of the liquid. This process by which bubbles form, grow and collapse is known as “cavitation”, and is the basis for ultrasound-assisted extraction (UAE) (Luque-Garcia & Luque de Castro, 2003). The cavitation process lasts about 400 μ s during which high temperatures and pressures, about 5000 °C and 1000 atm., respectively, can be witnessed (Azmir et al., 2013; Luque-Garcia & Luque de Castro, 2003).

2.4.2. Operational issues for ultrasound-assisted extraction

Two modes of the UAE system exist, namely bath and probe units. While the former is more generally used, two main disadvantages limit its reproducibility in extraction processes: (a) lack of

uniformity in ultrasound energy distribution, and (b) decline of power with time, so that the energy supplied to bath is wasted. On the contrary, ultrasonic probes are a better concept since their energy can be focused on specific sample zone yielding more efficient liquid cavitation (Luque-Garcia & Luque de Castro, 2003; Vinatoru, 2001). In pectin extraction investigations, probe units seem to be more popular in laboratory scale studies.

In implementing UAE effectively and efficiently, it is important to give proper consideration to the plant characteristics—including moisture content and particle size, the solvent, as well as the hardware conditions of the ultrasound system itself. Ultrasound system conditions will typically include temperature, pressure, frequency, and sonication time. The solvent-biomass ratio is also important since attenuation of the ultrasound intensity occurs with increasing solid particle contents (Wang & Weller, 2006).

Investigations on the efficacy of UAE for pectin extraction seem to be growing, probably spurred by a better understanding of the ultrasound technology itself. Bagherian et al. (2011), in their comparison of three different extraction techniques (CHE, MAE, and UAE) for pectin from grapefruit peels, found that intermittent sonication in a water bath rather than continuous sonication gave better yields. Further, the authors considered sonication time and bath temperatures to be the most important factors in the UAE process, with respective optimal values, 25 min and 70 °C. However, the yield (17.92% (w/w) db) by this process was lower than that from microwave process at its optimum (27.81% (w/w) db).

Wang et al. (2015) also attempted pectin recovery from grapefruit peel, reporting that, quantitatively, ultrasound-assisted heating extraction using a probe system gave better yield than conventional heating extraction (~16% increase) and required ~38% less time to give that much yield. Qualitatively, UAE allowed extraction to occur at a temperature 13.3 °C less than in conventional heating, which showed, upon image examination, better colour and more loosened microstructure compared to that extracted by CHE, although FT-IR analysis indicated insignificant difference in their chemical structures.

In other studies, the interactive effect of all four process variables—namely, solid-liquid ratio, pH, extraction time and temperature—were considered in the UAE extraction of pectin from pomegranate peels. The process was optimized using Box–Behnken response surface design coupled with numerical optimization technique. Results indicated that a system with 1:17.52 g/ml of solid-liquid ratio, 1.27 of pH, 28.31 min of extraction time and 61.90 °C of extraction temperature represented the optimum condition (Moorthy, Maran, Surya, Naganyashree, & Shivamathi, 2015). Another UAE of pectin from sisal waste was performed using an ultrasonic device with a probe unit (Prakash Maran & Priya, 2015). Ultrasonic power (50–70 W), extraction temperature (40–60 °C), extraction time (10–30 min), and solid-liquid ratio (20–40 g/ml) were the four factors considered for the Box–Behnken response surface experimental design, at three levels each. A yield prediction model based on these parameters was developed and its reliability validated empirically; maximum yield of 29.13% was obtained under conditions: ultrasonic power of 61 W, temperature of 50 °C, time of 26 min and SL ratio of 1:28 g/ml.

An increasing trend in extraction investigations has seen a synergistic use of two or more novel technologies. A case in point is the investigation by a group of researchers in China on sugar beet pulp, who not only obtained higher yield by an ‘ultrasound-/microwave-assisted acid method’ (abridged UMAAM), but also reported pectin with much higher M_w (636.20 vs. 295.95 kDa) in comparison to pectin obtained by traditional means (Peng et al., 2015). The configuration of the ultrasonic system was however not reported.

2.4.3. Benefits and drawbacks of ultrasound-assisted extraction

Of course, UAE has a number of advantages, most notably the reduced extraction time, reduced energy consumption and a relatively lower use of solvent (Azmir et al., 2013). Further, intrinsic benefits of this extraction technique as outlined by Chemat, Tomao, and Viot (2008) as related to polysaccharide extraction include: (1) more effective mixing and micro-mixing, (2) faster energy (heat) and mass transfer, (3) reduced thermal and concentration gradients and extraction temperature, (4) selective extraction, (5) reduced equipment size, (6) faster response to process extraction control, (7) faster start-up, (8) increased production, and (9) elimination of process steps.

On the downside, the fact that more concentration of dispersed phase results in attenuation of the ultrasound wave means that UAE does not greatly reduce solvent requirement after all (Wang & Weller, 2006). Another potential shortcoming is that effectiveness of ultrasound enhancing the yield and kinetics of pectin during recovery is biomass-specific plant. This means that yield varies and might not give output improvement for certain materials. Further, on the instrumentation aspect, the decline in ultrasound intensity away from the vicinity of the emitter means that uniformity might not be reached for all the materials dispersed in the solvent (Wang & Weller, 2006). However, if all these factors are carefully considered, UAE can well be the technique of choice for industrial extraction of pectin.

3. Future perspectives and concluding remarks

The market for pectin and other hydrocolloids is quite huge and is projected to grow (Phillips & Williams, 2009). Application of pectin are common within the food and non-food industries alike, with yet more applications being discovered. These uses have a direct relationship with some of the structural and functional properties of the polysaccharide, all of which are influenced by extraction method. Current pectin extraction process is well established; however, keeping up with growing demands means improvement in the process both with regards to speed of this operation and the predictability and repeatability of the products' physicochemical qualities.

As underlined by the present manuscript, a number of effective and efficient novel techniques are currently being examined for integration into the pectin extraction process, including microwave, ultrasound, subcritical water, and enzymes, with varying levels of successes. However, even though these techniques give quantitatively and qualitatively better products in the laboratory scale as batch operations, so far, poor and sometimes incomplete understanding of their applicability upon scale-up appears to retard their mainstream industrial translation where a continuous process is now more preferred. More studies comparable to those of Casas-Orozco et al. (2015) and Wiesenborn, Wang, Chang, and Schwarz (1999) are thus need for these novel techniques. Progress is expected as regards filling this scalability knowledge gap, at least from laboratory to pilot scale. Panouillé et al. (2006) attempted a mini pilot-scale of their enzymatic extraction process (0.5 l solvent), but there needs to be improvement in this regard to attract industrial contemplation and possibly future implementation.

Lastly, while this might not apply to larger specialty chemical/ingredient producers, some of these technologies are still prohibitively expensive for the newer and modest producers. But in the meantime, proper optimization of process parameters of these new approaches are needed. It might not be long before industry stakeholders begin embracing one or more of these methods to produce specialty pectins—most likely the integration of microwave heating—for rapid mass transfer (Ciriminna, Chavarría-Hernández, Inés Rodríguez Hernández, & Pagliaro, 2015). Another

focus of many research institutes and laboratories has been the identification and utilization of new fruit and vegetable waste streams, other than the industrially established once listed earlier, as raw materials for pectin production. These are all in view of meeting the ever-increasing demand for this versatile biopolymer.

Acknowledgement

The financial supports of the National Science and Engineering Research Council of Canada (NSERC) and Fonds de recherche du Québec – Nature et technologies (FRQNT) are gratefully acknowledged. The authors also wish to acknowledge the effort of Mr Sai Kranthi and Mr Jiby Kurian in reviewing the manuscript.

References

- Alexander, M. M., & Sulebele, G. A. (1973). Pectic substances in onion and garlic skins. *Journal of the Science of Food and Agriculture*, 24(5), 611–615.
- Almeida, E. A. M. S., Facchi, S. P., Martins, A. F., Nocchi, S., Schuquel, I. T. A., Nakamura, C. V., et al. (2015). Synthesis and characterization of pectin derivative with antitumor property against Caco-2 colon cancer cells. *Carbohydrate Polymers*, 115(0), 139–145.
- Anton, A. A., & Artfield, S. D. (2008). Hydrocolloids in gluten-free breads: A review. *International Journal of Food Sciences and Nutrition*, 59(1), 11–23.
- Azmir, J., Zaidul, I. S. M., Rahman, M. M., Sharif, K. M., Mohamed, A., Sahena, F., et al. (2013). Techniques for extraction of bioactive compounds from plant materials: A review. *Journal of Food Engineering*, 117(4), 426–436.
- Bagherian, H., Zokaee Ashtiani, F., Fouladitajar, A., & Mohtashamy, M. (2011). Comparisons between conventional, microwave- and ultrasound-assisted methods for extraction of pectin from grapefruit. *Chemical Engineering and Processing: Process Intensification*, 50(11–12), 1237–1243.
- Bierhalz, A. C. K., da Silva, M. A., & Kieckbusch, T. G. (2012). Natamycin release from alginate/pectin films for food packaging applications. *Journal of Food Engineering*, 110(1), 18–25.
- Brown, L., Rosner, B., Willett, W. W., & Sacks, F. M. (1999). Cholesterol-lowering effects of dietary fiber: A meta-analysis. *The American Journal of Clinical Nutrition*, 69(1), 30–42.
- Brunner, G. (2009). Near critical and supercritical water. Part I. Hydrolytic and hydrothermal processes. *The Journal of Supercritical Fluids*, 47(3), 373–381.
- Burnside, E. (2014). Chapter 21-Hydrocolloids and gums as encapsulating agents. In A. G. Gaonkar, N. Vasisht, A. R. Khare, & R. Sobel (Eds.), *Microencapsulation in the food industry* (pp. 241–252). San Diego: Academic Press.
- Caffall, K. H., & Mohnen, D. (2009). The structure, function, and biosynthesis of plant cell wall pectic polysaccharides. *Carbohydrate Research*, 344(14), 1879–1900.
- Casas-Orozco, D., Villa, A. L., Bustamante, F., & González, L.-M. (2015). Process development and simulation of pectin extraction from orange peels. *Food and Bioprocess Processing*, 96, 86–98.
- Chemat, F., Tomao, V., & Viot, M. (2008). *Ultrasound-assisted extraction in food analysis Handbook of food analysis instruments*. CRC Press.
- Chen, H.-m., Fu, X., & Luo, Z.-g. (2015). Properties and extraction of pectin-enriched materials from sugar beet pulp by ultrasonic-assisted treatment combined with subcritical water. *Food Chemistry*, 168(0), 302–310.
- Cho, Y.-J., & Hwang, J.-K. (2000). Modeling the yield and intrinsic viscosity of pectin in acidic solubilization of apple pomace. *Journal of Food Engineering*, 44(2), 85–89.
- Ciriminna, R., Chavarría-Hernández, N., Inés Rodríguez Hernández, A., & Pagliaro, M. (2015). Pectin: A new perspective from the biorefinery standpoint. *Biofuels, Bioprocesses and Biorefining*, 9(4), 368–377.
- Dominiak, M., Søndergaard, K. M., Wichmann, J., Vidal-Melgosa, S., Willats, W. G. T., Meyer, A. S., et al. (2014). Application of enzymes for efficient extraction, modification, and development of functional properties of lime pectin. *Food Hydrocolloids*, 40, 273–282.
- El-Nawawi, S. A., & Shehata, F. R. (1987). Extraction of pectin from Egyptian orange peel. Factors affecting the extraction. *Biological Wastes*, 20(4), 281–290.
- Endress, H. U. (2011). Chapter 8 Pectins: Production, properties and applications renewable resources for functional polymers and Biomaterials: Polysaccharides, proteins and polyesters (pp. 210–260). The Royal Society of Chemistry.
- Fishman, M. L., Chau, H. K., Cooke, P. H., & Hotchkiss, A. T., Jr. (2008). Global structure of microwave-assisted flash-extracted sugar beet pectin. *Journal of Agricultural and Food Chemistry*, 56(4), 1471–1478.
- Fishman, M. L., Chau, H. K., Hoagland, P., & Ayyad, K. (1999). Characterization of pectin, flash-extracted from orange albedo by microwave heating, under pressure. *Carbohydrate Research*, 323(1–4), 126–138.
- Fishman, M. L., Chau, H. K., Hoagland, P. D., & Hotchkiss, A. T. (2006). Microwave-assisted extraction of lime pectin. *Food Hydrocolloids*, 20(8), 1170–1177.
- Fissore, E. N., Ponce, N. M., Wider, E. A., Stortz, C. A., Gerschenson, L. N., & Rojas, A. M. (2009). Commercial cell wall hydrolytic enzymes for producing pectin-enriched products from butternut (Cucurbita moschata, Duchesne ex Poiret). *Journal of Food Engineering*, 93(3), 293–301.
- Gentilini, R., Bozzini, S., Munarin, F., Petrini, P., Visai, L., & Tanzi, M. C. (2014). Pectins

- from *Aloe Vera*: Extraction and production of gels for regenerative medicine. *Journal of Applied Polymer Science*, 131(2). <http://dx.doi.org/10.1002/app.39760>.
- Hasselwander, O. (2008). Pectin — Health Benefits as a Dietary Fibre and Beyond. Paper presented at the Gums and Stabilisers for the Food Industry 14, Cambridge, UK.
- Hawthorne, S. B., Grabanski, C. B., Martin, E., & Miller, D. J. (2000). Comparisons of Soxhlet extraction, pressurized liquid extraction, supercritical fluid extraction and subcritical water extraction for environmental solids: Recovery, selectivity and effects on sample matrix. *Journal of Chromatography A*, 892(1–2), 421–433.
- Ibanez, E., Kubátová, A., Senoráns, F. J., Cavero, S., Reglero, G., & Hawthorne, S. B. (2003). Subcritical water extraction of antioxidant compounds from rosemary plants. *Journal of Agricultural and Food Chemistry*, 51(2), 375–382.
- Jensen, S. V., Sørensen, S. O., Rolin, C. (2013). US8592575 B2: USPTO.
- Jeong, H.-S., Kim, H.-Y., Ahn, S. H., Oh, S. C., Yang, I., & Choi, I.-G. (2014). Optimization of enzymatic hydrolysis conditions for extraction of pectin from rapeseed cake (*Brassica napus* L.) using commercial enzymes. *Food Chemistry*, 157, 332–338.
- Kai, P., Yan, Z., Sijin, W., Xiaojun, L., & Xiaosong, H. (2008). Effect of microwave drying pretreatment on extraction of pectin from apple pomace. *Transactions of the Chinese Society of Agricultural Engineering*, 2008(7).
- Kalapathy, U., & Proctor, A. (2001). Effect of acid extraction and alcohol precipitation conditions on the yield and purity of soy hull pectin. *Food Chemistry*, 73(4), 393–396.
- Kertesz, Z. I. (1951). *The pectic substances*. New York: Interscience Publishers.
- Khajavi, S. H., Kimura, Y., Oomori, T., Matsuno, R., & Adachi, S. (2005). Degradation kinetics of monosaccharides in subcritical water. *Journal of Food Engineering*, 68(3), 309–313.
- Kratchanova, M., Panchev, I., Pavlova, E., & Shtereva, L. (1994). Extraction of pectin from fruit materials pretreated in an electromagnetic field of super-high frequency. *Carbohydrate Polymers*, 25(3), 141–144.
- Kravtchenko, T. P., Arnould, I., Voragen, A. G. J., & Pilnik, W. (1992). Improvement of the selective depolymerization of pectic substances by chemical β -elimination in aqueous solution. *Carbohydrate Polymers*, 19(4), 237–242.
- Kulkarni, S. G., & Vijayanand, P. (2010). Effect of extraction conditions on the quality characteristics of pectin from passion fruit peel (*Passiflora edulis* f. *flavicarpa* L.). *LWT - Food Science and Technology*, 43(7), 1026–1031.
- Leonelli, C., Veronesi, P., & Cravotto, G. (2013). Microwave-assisted Extraction: An introduction to dielectric heating. In F. Chemat, & G. Cravotto (Eds.), *Microwave-assisted extraction for bioactive compounds* (pp. 1–14). US: Springer.
- Letellier, M., & Budzinski, H. (1999). Microwave assisted extraction of organic compounds. *Analisis*, 27(3), 259–270.
- Li, J. M., & Nie, S. P. (2016). The functional and nutritional aspects of hydrocolloids in foods. *Food Hydrocolloids*, 53, 46–61.
- Liu, L. S., Fishman, M. L., & Hicks, K. B. (2007). Pectin in controlled drug delivery - A review. *Cellulose*, 14(1), 15–24.
- Loncin, M., & Merson, R. L. (1979). Equations related to the transfer of mass, heat, and momentum. In M. L. L. Merson (Ed.), *Food engineering. Principles and selected applications* (pp. 11–40). Academic Press.
- Lopes da Silva, J. A., & Rao, M. A. (2006). Pectins: Structure, functionality, and uses. In A. M. Stephen, G. O. Phillips, & P. A. Williams (Eds.), *Food polysaccharides and their applications* (2nd ed.). Boca Raton, FL: CRC/Taylor & Francis.
- Luque-Garcia, J. L., & Luque de Castro, M. D. (2003). Ultrasound: A powerful tool for leaching. *TrAC Trends in Analytical Chemistry*, 22(1), 41–47.
- Maran, J. P., & Prakash, K. A. (2015). Process variables influence on microwave assisted extraction of pectin from waste Carica papaya L. peel. *International Journal of Biological Macromolecules*, 73, 202–206.
- Maran, J. P., & Priya, B. (2015). Ultrasound-assisted extraction of pectin from sisal waste. *Carbohydrate Polymers*, 115(0), 732–738.
- Matora, A. V., Korshunova, V. E., Shkodina, O. G., Zhemerichkin, D. A., Pritchkina, N. M., & Morris, E. R. (1995). The application of bacterial enzymes for extraction of pectin from pumpkin and sugar beet. *Food Hydrocolloids*, 9(1), 43–46.
- Maxwell, E. G., Belshaw, N. J., Waldron, K. W., & Morris, V. J. (2012). Pectin — An emerging new bioactive food polysaccharide. *Trends in Food Science & Technology*, 24(2), 64–73.
- May, C. D. (1990). Industrial pectins: Sources, production and applications. *Carbohydrate Polymers*, 12(1), 79–99.
- Michel, F., Thibault, J.-F., Mercier, C., Heitz, F., & Poullaud, F. (1985). Extraction and characterization of pectins from sugar beet pulp. *Journal of Food Science*, 50(5), 1499–1500. <http://onlinelibrary.wiley.com/doi/10.1111/j.1365-2621.1985.tb10512.x/abstract>.
- Minkov, S., Minchev, A., & Paev, K. (1996). Modelling of the hydrolysis and extraction of apple pectin. *Journal of Food Engineering*, 29(1), 107–113.
- Miyamoto, A., & Chang, K. C. (1992). Extraction and physicochemical characterization of pectin from sunflower head residues. *Journal of Food Science*, 57(6), 1439–1443.
- Moorthy, I. G., Maran, J. P., Surya, S. M., Naganyashree, S., & Shivamathi, C. S. (2015). Response surface optimization of ultrasound assisted extraction of pectin from pomegranate peel. *International Journal of Biological Macromolecules*, 72(0), 1323–1328.
- Muzzarelli, R. A. A., Boudrant, J., Meyer, D., Manno, N., DeMarchis, M., & Paoletti, M. G. (2012). Current views on fungal chitin/chitosan, human chitinases, food preservation, glucans, pectins and inulin: A tribute to Henri Brannon, precursor of the carbohydrate polymers science, on the chitin bicentennial. *Carbohydrate Polymers*, 87(2), 995–1012.
- Naghshineh, M., Olsen, K., & Georgiou, C. A. (2013). Sustainable production of pectin from lime peel by high hydrostatic pressure treatment. *Food Chemistry*, 136(2), 472–478.
- Norton, I. T., Fryer, P., & Moore, S. (2006). Product/Process integration in food manufacture: Engineering sustained health. *AIChE Journal*, 52(5), 1632–1640.
- Pagán, J., Ibarz, A., Llorca, M., Pagán, A., & Barbosa-Cánovas, G. V. (2001). Extraction and characterization of pectin from stored peach pomace. *Food Research International*, 34(7), 605–612.
- Panouillé, M., Thibault, J.-F., & Bonnin, E. (2006). Cellulase and protease preparations can extract pectins from various plant byproducts. *Journal of Agricultural and Food Chemistry*, 54(23), 8926–8935.
- Peng, X.-Y., Mu, T.-H., Zhang, M., Sun, H.-N., Chen, J.-W., & Yu, M. (2015). Optimization of production yield by ultrasound-/microwave-assisted acid method and functional property of pectin from sugar beet pulp. *International Journal of Food Science & Technology*, 50(3), 758–765.
- Phillips, G. O., & Williams, P. A. (2009). *Introduction to food hydrocolloids Handbook of hydrocolloids* (2nd ed.). Woodhead Publishing.
- Pinelo, M., Sineiro, J., & Núñez, M. A. J. (2006). Mass transfer during continuous solid–liquid extraction of antioxidants from grape byproducts. *Journal of Food Engineering*, 77(1), 57–63.
- Prakash Maran, J., Sivakumar, V., Thirugnanasambandham, K., & Sridhar, R. (2013). Optimization of microwave assisted extraction of pectin from orange peel. *Carbohydrate Polymers*, 97(2), 703–709.
- Prakash Maran, J., Swathi, K., Jeevitha, P., Jayalakshmi, J., & Ashvini, G. (2015). Microwave-assisted extraction of pectic polysaccharide from waste mango peel. *Carbohydrate Polymers*, 123, 67–71.
- Pitchkina, N. M., Markina, O. A., & Rumyantseva, G. N. (2008). Pectin extraction from pumpkin with the aid of microbial enzymes. *Food Hydrocolloids*, 22(1), 192–195.
- Puri, M., Sharma, D., & Barrow, C. J. (2012). Enzyme-assisted extraction of bioactives from plants. *Trends in Biotechnology*, 30(1), 37–44.
- Rababah, T. M., Al-u'datt, M. H., & Brewer, S. (2015). *Chapter 82-Jam processing and impact on composition of active compounds A2-oreedy, victor processing and impact on active components in food* (pp. 681–687). San Diego: Academic Press.
- Rabbani, G. H., Tekka, T., Saha, S., Zaman, B., Majid, N., Khatun, M., et al. (2004). Green banana and pectin improve small intestinal permeability and reduce fluid loss in Bangladeshi children with persistent diarrhea. *Digestive Diseases and Sciences*, 49(3), 475–484.
- Rabbani, G. H., Tekka, T., Zaman, B., Majid, N., Khatun, M., & Fuchs, G. J. (2001). Clinical studies in persistent diarrhea: Dietary management with green banana or pectin in Bangladeshi children. *Gastroenterology*, 121(3), 554–560.
- Ramaswamy, H. S., & Basak, S. (1992). Pectin and raspberry concentrate effects on the rheology of stirred commercial yogurt. *Journal of Food Science*, 57(2), 357–360.
- Rhein-Knudsen, N., Ale, M. T., & Meyer, A. S. (2015). Seaweed hydrocolloid Production: An update on enzyme assisted extraction and modification technologies. *Marine Drugs*, 13(6), 3340–3359.
- Richardson, J. F., Harker, J. H., & Backhurst, J. R. (2002). *Coulson and Richardson's chemical engineering volume 2-Particle technology and separation processes* (5th ed.). Elsevier.
- Ridley, B. L., O'Neill, M. A., & Mohnen, D. (2001). Pectins: Structure, biosynthesis, and oligogalacturonide-related signaling. *Phytochemistry*, 57(6), 929–967.
- Routray, W., & Orsat, V. (2012). Microwave-assisted extraction of flavonoids: A review. *Food and Bioprocess Technology*, 5(2), 409–424.
- Schmidt, U. S., Koch, L., Rentschler, C., Kurz, T., Endreß, H. U., & Schuchmann, H. P. (2015). Effect of molecular weight reduction, acetylation and esterification on the emulsification properties of citrus pectin. *Food Biophysics*, 10, 217–227. <http://dx.doi.org/10.1007/s11483-014-9380-1>.
- Sowbhagya, H. B., & Chitra, V. N. (2010). Enzyme-assisted extraction of flavorings and colorants from plant materials. *Critical Reviews in Food Science and Nutrition*, 50(2), 146–161.
- Srinivas, K., King, J. W., Monrad, J. K., Howard, L. R., & Hansen, C. M. (2009). Optimization of subcritical fluid extraction of bioactive compounds using Hansen solubility parameters. *Journal of Food Science*, 74(6), E342–E354. <http://dx.doi.org/10.1111/j.1750-3841.2009.01251.x>.
- Thirugnanasambandham, K., Sivakumar, V., & Prakash Maran, J. (2014). Process optimization and analysis of microwave assisted extraction of pectin from dragon fruit peel. *Carbohydrate Polymers*, 112(0), 622–626.
- Tromp, R. H., de Kruij, C. G., van Eijk, M., & Rolin, C. (2004). On the mechanism of stabilisation of acidified milk drinks by pectin. *Food Hydrocolloids*, 18(4), 565–572.
- Ueno, H., Tanaka, M., Hosino, M., Sasaki, M., & Goto, M. (2008). Extraction of valuable compounds from the flavedo of Citrus junos using subcritical water. *Separation and Purification Technology*, 62(3), 513–516.
- Veggi, P., Martinez, J., & Meireles, M. A. (2013). Fundamentals of microwave extraction. In F. Chemat, & G. Cravotto (Eds.), *Microwave-assisted extraction for bioactive compounds* (pp. 15–52). US: Springer.
- Venkatesh, M. S., & Raghavan, G. S. V. (2004). An overview of microwave processing and dielectric properties of agri-food materials. *Biosystems Engineering*, 88(1), 1–18.
- Vinatoru, M. (2001). An overview of the ultrasonically assisted extraction of bioactive principles from herbs. *Ultrasonics Sonochemistry*, 8(3), 303–313.
- Voss, W. A. G. (1974, 10–13 Sept. 1974). Industrial Microwave Applications. Paper presented at the Microwave Conference, 1974. 4th European.
- Wang, X., Chen, Q., & Lü, X. (2014). Pectin extracted from apple pomace and citrus peel by subcritical water. *Food Hydrocolloids*, 38(0), 129–137.
- Wang, S., Chen, F., Wu, J., Wang, Z., Liao, X., & Hu, X. (2007). Optimization of pectin

- extraction assisted by microwave from apple pomace using response surface methodology. *Journal of Food Engineering*, 78(2), 693–700.
- Wang, W., Ma, X., Xu, Y., Cao, Y., Jiang, Z., Ding, T., et al. (2015). Ultrasound-assisted heating extraction of pectin from grapefruit peel: Optimization and comparison with the conventional method. *Food Chemistry*, 178(0), 106–114.
- Wang, L., & Weller, C. L. (2006). Recent advances in extraction of nutraceuticals from plants. *Trends in Food Science & Technology*, 17(6), 300–312.
- WHO/FAO. (1981). Evaluation of certain food additives (Twenty-fifth report of the joint FAO/WHO expert committee on food additives). In FAO/WHO (Ed.), *WHO technical report series*. Geneva, Switzerland: World Health Organization.
- Wiesenborn, D. P., Wang, J., Chang, K. C., & Schwarz, J. G. (1999). Comparison of continuous and batch processes for pectin extraction from sunflower heads. *Industrial Crops and Products*, 9(3), 171–181.
- Wikiera, A., Miika, M., & Grabacka, M. (2015). Multicatalytic enzyme preparations as effective alternative to acid in pectin extraction. *Food Hydrocolloids*, 44, 156–161.
- Yamada, H., Kiyohara, H., & Matsumoto, T. (2003). Recent studies on possible functions of bioactive pectins and pectic polysaccharides from medicinal herbs on health care. In F. Voragen, H. Schols, & R. Visser (Eds.), *Advances in pectin and pectinase research* (pp. 481–490). Netherlands: Springer.
- Yanakiyeva, I., Kussovski, V., & Kratchanova, M. (2012). Isolation, characterization and modification of citrus pectins. *Journal of BioScience and Biotechnology*, 1(3), 223–233.
- Zakaria, S. M., & Kamal, S. M. M. (2015). Subcritical water extraction of bioactive compounds from plants and Algae: Applications in pharmaceutical and food ingredients. *Food Engineering Reviews*, 1–12.
- Zhao, W., Guo, X., Pang, X., Gao, L., Liao, X., & Wu, J. (2015). Preparation and characterization of low methoxyl pectin by high hydrostatic pressure-assisted enzymatic treatment compared with enzymatic method under atmospheric pressure. *Food Hydrocolloids*, 50, 44–53.
- Zhuang, Y., Sterr, J., Kulozik, U., & Gebhardt, R. (2015). Application of confocal Raman microscopy to investigate casein micro-particles in blend casein/pectin films. *International Journal of Biological Macromolecules*, 74(0), 44–48.
- Zykwinska, A., Boiffard, M.-H., Kontkanen, H., Buchert, J., Thibault, J.-F., & Bonnin, E. (2008). Extraction of green labeled pectins and pectic oligosaccharides from plant byproducts. *Journal of Agricultural and Food Chemistry*, 56(19), 8926–8935.